



## Short communication

High surface electrochemical support based on Sb-doped SnO<sub>2</sub>

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## HIGHLIGHTS

- ATO support is prepared by sol–gel with dodecylamine as template.
- The resulting powder has the highest specific surface area until now reported.
- Electrical conductivity value is comparable to the typically used carbon.
- ATO support showed great stability to high overpotentials in acid media.
- ATO has strong potential for using in several electrochemical applications.

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## ABSTRACT

Sb-doped SnO<sub>2</sub> (ATO) support is prepared by sol–gel method in the presence of dodecylamine as template. The synthesized powder presents the highest specific surface area until now reported (216.7 m<sup>2</sup> g<sup>−1</sup>) with high electrical conductivity (0.202 S cm<sup>−1</sup>). The durability test accomplished by cyclic voltammetry in acid media (100 cycles between 0 and 1.7 V vs NHE) demonstrates that the ATO support maintains significantly its stability and the performance of the tested electrocatalyst compared to Vulcan XC-72. The ATO material is a promising support that can be used in several electrochemical applications where the use of carbon is not suitable.

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## 1. Introduction

Tin dioxide, SnO<sub>2</sub>, belongs to the family of transition metal dioxide compounds with rutile structures. SnO<sub>2</sub>-supported Pt and Pd metals are interesting catalyst systems for various reactions, such as the low-temperature oxidation of CO and methane [1,2]. SnO<sub>2</sub> has also been proposed as a support material for fuel cell and electrolysis electrocatalysts because of its chemical properties; it adsorbs OH species at low potentials and/or induces an electronic effect with Pt catalysts [3,4]. Undoped tin dioxide is a wide bandgap semiconductor ( $E_g \approx 3.6$  eV) with electrical resistivity varying from 10 to 10<sup>6</sup> Ω cm, depending on the temperature and the stoichiometry of the oxide [5]. The

electrical resistivity was found to drastically decrease to 10<sup>−2</sup>–10<sup>−3</sup> Ω cm upon doping SnO<sub>2</sub> with Sb<sup>5+</sup> [6–8]. Other materials have been investigated such as Ebonex<sup>®</sup> and used as a catalyst support for the oxygen reduction and evolution reaction [9–12]; however, a major detriment for use in practical support applications resides in its low surface area compared to Vulcan XC-72 [13].

Recent studies have shown the potential use of ATO material. Santos et al. [14] electrodeposited platinum microparticles on Sb-doped SnO<sub>2</sub> (ATO) thin films and tested their activity for methanol electro-oxidation. The crystallite size of ATO-supported Pt was in the range of 8.5–12 nm. These results suggest that tin oxide can be a good matrix for Pt (or Pt alloys) catalyst dispersion for applications in DMFC. Lee et al. [15] deposited Pt colloidal particles on ATO nanoparticles with various degrees of Pt loading and investigated their electrocatalytic activity and stability for methanol and ethanol oxidation reactions. The electrical conductivities of undoped and Sb–SnO<sub>2</sub> were 0.0028 and 0.11 S cm<sup>−1</sup>,

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respectively. The specific surface area of the ATO from a BET analysis was  $99.7 \text{ m}^2 \text{ g}^{-1}$ . To our knowledge Sb– $\text{SnO}_2$  has a surface area less than  $100 \text{ m}^2 \text{ g}^{-1}$  lower than Vulcan XC-72. Hagemeyer et al. [16] investigated a variety of methods for the preparation of high-surface-area tin oxide. BET analysis of the surface area showed values between 43 and  $100 \text{ m}^2 \text{ g}^{-1}$  by a variety of methods after calcinations in the temperature range of 300–500 °C, indicating the presence of mesopores in the ATO support [17]. The synthesis of ATO with a high surface area (up to  $100 \text{ m}^2 \text{ g}^{-1}$ ) is a primary requirement for its use as a catalyst/electrocatalyst support for different chemical and electrochemical reactions such as oxygen evolution reaction by water. The support provides a physical surface for the dispersion of small particles of the active phase, which is necessary for achieving high surface area and to provide good electronic conductivity. Besides, a high stability at the anodic potential is required. A variety of techniques have been used to synthesize tin oxide nanoparticles, including Sol–gel technique [7] that has attracted the most attention for the preparation of Sb-doped  $\text{SnO}_2$  because of several advantages, such as excellent homogeneity, ease of controlling the doping level, ability to coat large areas and complex shapes and a low processing cost [18–20]. In this work, Sb-doped  $\text{SnO}_2$  (ATO) support was prepared by a novel route Sol–gel method in the presence of dodecylamine as template, resulting in a powder with high specific surface area ( $216.7 \text{ m}^2 \text{ g}^{-1}$ ) and electrical conductivity ( $0.202 \text{ S cm}^{-1}$ ).

## 2. Experimental

### 2.1. Synthesis of ATO

ATO begins with the synthesis of the precursor solution using Tin (IV) *tert*-butoxide (Aldrich,  $\geq 98\%$ ), anhydrous ethanol (Aldrich,  $\geq 99.7\%$ ),  $\text{HNO}_3$  (Aldrich), dodecylamine (Aldrich,  $\geq 99\%$ ), distilled water and antimony (III) ethoxide (Aldrich) in a tri-necked flask. All of the chemical reagents used in this experiment are of analytical grade.  $\text{Sn}^{4+}$  and  $\text{Sb}^{3+}$  precursors in a molar ratio of 90:10 (Sn:Sb) are mixed in ethanol under an inert atmosphere ( $\text{N}_2$ ) by magnetic stirring for 30 min. The final pH value of this solution is 2.5. Subsequently, for the hydrolysis reaction, the solution was added to 0.1 M nitric acid aqueous solution as the catalyst and 84 mM dodecylamine as surfactant, with a gelation time ( $t_g$ ) of 4 h at 5 °C. Then, the resulting gels were kept at room temperature for one day, filtered and subsequently washed with deionized water at 80 °C. After the resulting gel powder was crushed in an agate mortar, it underwent thermal processing, starting at  $T = 110 \text{ °C}$  for 18 h at heating rate of  $2 \text{ °C min}^{-1}$ . After at  $T = 500 \text{ °C}$  for 12 h at heating rate of  $1.5 \text{ °C min}^{-1}$ .

### 2.2. Physicochemical characterization

XRD was performed on the dry support powders of ATO using an X-pert MPD Philips diffractometer that used the K $\alpha$  line of copper

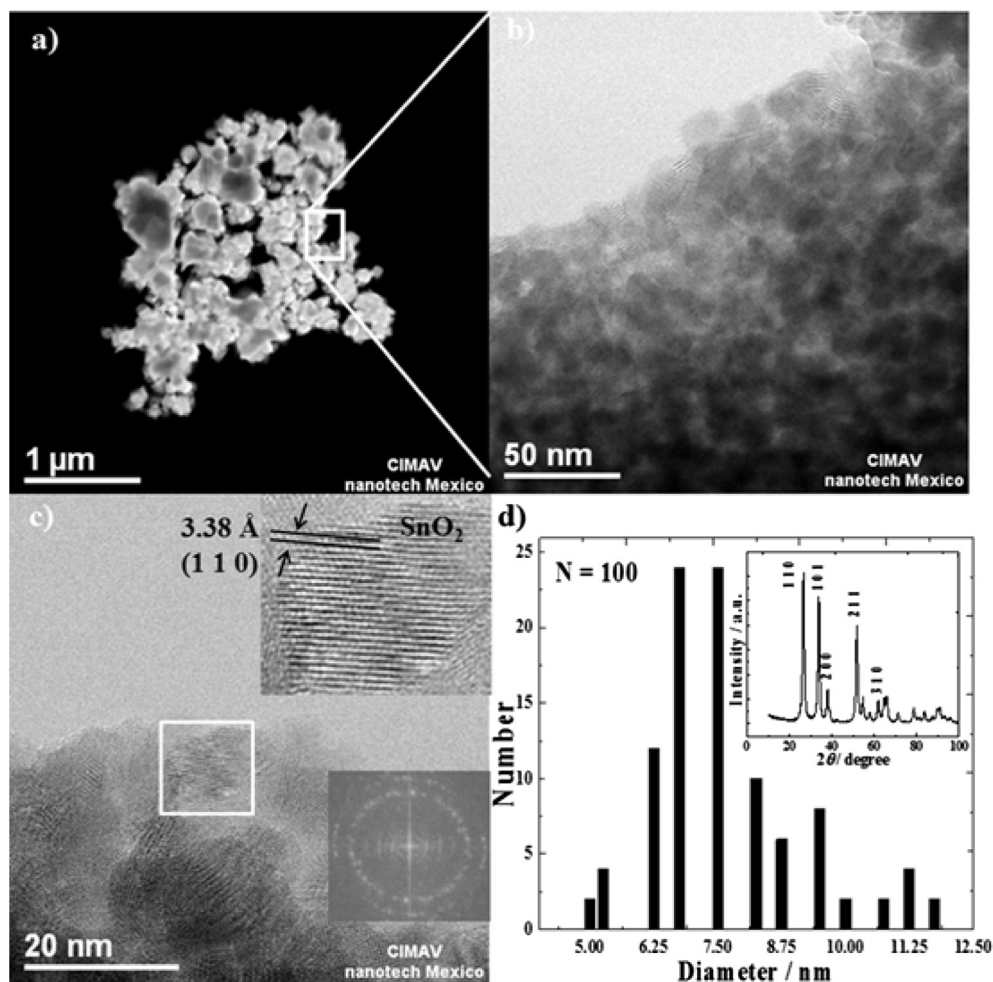


Fig. 1. TEM micrographs of ATO support and particle size distribution analysis of ATO calcinated for 12 h at 500 °C. d) Inset X-ray diffraction pattern of Sb-doped  $\text{SnO}_2$  (ATO).

(CuK $\alpha$ ) as the radiation source. The diffractometer operated at 40 kV and 20 mA with a step time of 0.2° min<sup>-1</sup>. The morphology of the supports was investigated using a JEM2200FS, field emission high-resolution transmission electron microscope (TEM) operated at 200 kV. The specific surface area of the supports was evaluated by multipoint Brunauer–Emmett–Teller (BET) analysis of the nitrogen adsorption isotherms recorded on a surface area analyzer (Autosorb iQ2). Electrical conductivity measurements for the materials were obtained through the four-point method with an Agilent 4338B milliohmmeter imposing a current of 100 mA.

### 2.3. Electrochemical characterization

Cyclic voltammograms were obtained in a conventional three-electrode electrochemical cell using a glass carbon electrode (3 mm diameter) as working electrode, platinum wire as counter electrode, and a 0.5 M Hg/Hg<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>SO<sub>4</sub> solution as the reference electrode. Electrochemical measurements were all recorded and reported versus the normal hydrogen electrode (NHE). Electrochemical experiments were performed with an Eco ChemieAutolab. A solution of 0.5 M H<sub>2</sub>SO<sub>4</sub> was used as the supporting electrolyte and was purged with nitrogen gas before the measurements.

## 3. Results and discussion

Inset in Fig. 1(d) shows the obtained diffraction patterns of the ATO support. From this analysis, it was possible to identify the most intense peaks at  $2\theta = 28^\circ$  and  $2\theta = 34^\circ$ , to the preferential plane (110) and (101), respectively, corresponding to the tetrahedral rutile structure (JCPDS 41-1445). The mean crystallite size was estimated from the broadening of the main peaks (110) using the Debye–Scherrer equation. An average crystal size of 5–6 nm was obtained for the ATO support. These sizes are smaller than the  $20 \pm 7$  nm reported for commercial ATO supports [21]. Fig. 1 also shows the TEM micrographs; spherical aggregates and networks can be seen. A careful analysis of several micrographs allows the estimation of the mean diameters of primary particles (Fig. 1(d)). In addition, the electron diffraction pattern (inset at 20 nm magnification) showed good crystallinity of ATO particles. The average crystal size was 6.65 nm. The mean sizes were comparable with the results obtained by XRD. Moreover, the interplanar distance in the direction (100) obtained by TEM images is 3.38 Å, which is in agreement with the estimated from XRD (Inset Table in Fig. 2(b)). The surface area, pore volume and size pore of the ATO were estimated through the BET method and are shown in Fig. 2; the obtained values of 216.73 m<sup>2</sup> g<sup>-1</sup>, and 0.276 cm<sup>3</sup> g<sup>-1</sup> and 6.53 nm, were significantly higher than the 1.17 m<sup>2</sup> g<sup>-1</sup> and 0.01 cm<sup>3</sup> g<sup>-1</sup> values reported for Ebonex<sup>®</sup> and comparable to the values for Carbon Vulcan XC-72 [22]. The analysis of pore size distribution indicated the presence of mesopores in the ATO support. It is remarkable that the surface area value obtained for the ATO support is the highest reported and that it provides a suitable, effective method for the dispersion of different catalytic materials that could dramatically increase performance compared to commercially available methods using Ebonex<sup>®</sup> and Carbon Vulcan supports. This high surface area could be due to the template used during synthesis, which generates a micellar structure than then is coated with the ATO precursors, when the surfactant is eliminated a mesoporous structure in ATO support was created. The surface area is even larger than the newly obtained by Jianqi Fan et al. [23], in which Pluronic block copolymer surfactant F127 were used as template, however only 94.4 m<sup>2</sup> g<sup>-1</sup> surface area was reached, with 3.7 nm of pore size. The difference in pore diameter obtained in both works could be explained by the difference between steps from preparation method. In this work, synthesis method included

an aging period during one day, which allowed maintaining similar pore diameter of the original micelle, while in the previous reported [23] certain micelle contraction occurred with solvent evaporation during dip-coating on the substrate.

In Fig. 2(a) and (b) the N<sub>2</sub> adsorption–desorption isotherms of the ATO and Carbon Vulcan XC-72 supports are shown. The N<sub>2</sub> adsorption–desorption isotherms for the ATO support are classified according to the IUPAC as type IV, with a typical H1-hysteresis loop [24,25] usually associated with an adsorption process on mesoporous solid associated with irreversible phenomena of capillary-evaporation into the uniform pores of ATO, in this case for the relative pressure  $P/P_0$  mainly in the range of 0.6–0.9, suggesting a very sharp pore size distribution at a mean value of about 6.53 nm [25,26]. In contrast, the isotherm of Vulcan XC-72 is type II, characteristic of the physical adsorption of gas by a non-porous or macroporous solid, with mono- and multilayer adsorption [23,26].

The electrical conductivity data of the ATO powder was obtained by the four-point method (Inset Fig. 2.). The electrical conductivity was 0.2022 S cm<sup>-1</sup>, which is slightly higher than the reported value of undoped and Sn-doped SnO<sub>2</sub> (0.1121 S cm<sup>-1</sup>) by Lee et al. [8,15] indicating that ATO has good electrical conductivity properties and could be used as a support for some catalysts. The electrical

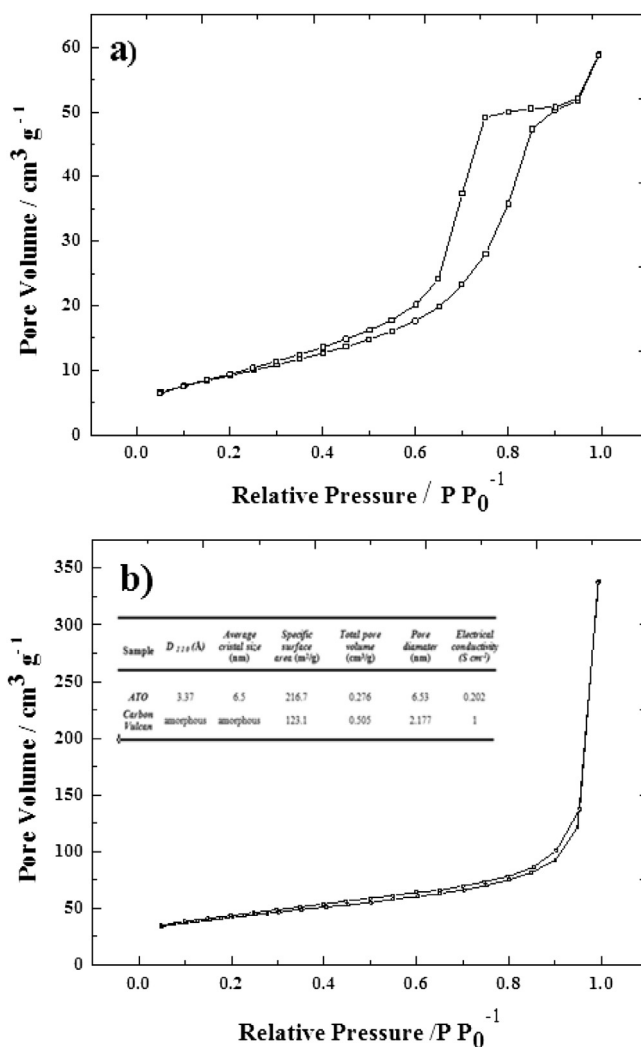


Fig. 2. Adsorption and desorption isotherms for a) ATO and b) Carbon Vulcan XC-72 supports. Inset Table: Surface area, total pore volume, pore diameter and electrical conductivity of ATO powders calculated for 12 h at 500 °C.

conductivity values are lower than the Carbon Vulcan; however, the doping process is performed to increase electrical conductivity. The electronic conductivity of Sb-doped  $\text{SnO}_2$  nanoparticles is well known to be dependent on the amount and oxidation state of Sb ( $\text{Sb}^{5+}$  and  $\text{Sb}^{3+}$ ) in the  $\text{SnO}_2$  lattice. A possible competence exists between these two oxidation states with increase the relative content of Sb in  $\text{SnO}_2$ . At low doping levels,  $\text{Sb}^{5+}$  species dominate and the substitution of  $\text{Sn}^{4+}$  by n-type dopant  $\text{Sb}^{5+}$  would generate more oxygen vacancies allowing an increase in the conductivity. In contrast, when the amount of Sb is increased,  $\text{Sb}^{5+}$  species gradually are replaced by  $\text{Sn}^{3+}$  as a compensation of oxygen vacancies (donor sites) inducing the p-type doping with an increase of the resistivity [27].

To evaluate the electrochemical stability of the ATO as a support, 100 cycles were carried out between 0 and 1.7 V vs. NHE in acid media. The material was prepared through a mechanical mix of ATO and 20% Pt black (Johnson Matthey) Pt/ATO. For comparison purposes, the same procedure was performed with carbon Vulcan XC-72, Pt/C. Fig. 3 shows the voltammetric profiles in acid media for 1) Pt/C and 2) Pt/ATO a) before and b) after the stability test. In both cases, the typical electrochemical response of platinum material is demonstrated. Observed peaks are clearly related to the adsorption and desorption of hydrogen as well as the formation and reduction

of platinum oxides. When examining the behavior of ATO as support, no appreciable change in the shape of the voltammogram before and after the stability test was found. The electrochemical surface area (ESA) of Pt was estimated from the charge ( $Q_H = 210 \mu\text{C cm}^{-2}$ ) to oxidize a full monolayer of adsorbed hydrogen atoms before and after the stability test. ESA value suffers a slight decrease of less than 10%. In contrast, when using Carbon Vulcan as the support, there is a clear change in the shape of the profile. A dramatic increase in the capacitance in the double layer region was observed in addition to the appearance of two redox peaks located at 0.5 V and 0.6 V related to the quinone–hydroquinone (Q/QH<sub>2</sub>) pair redox. Both phenomena are related to the oxidation of carbon Vulcan [8]. Furthermore, ESA value drops significantly. Based on these data, we can say that the ATO is a promising support for use in a large number of electrochemical applications.

#### 4. Conclusions

In summary, Sb-doped  $\text{SnO}_2$  (ATO) prepared by sol–gel method exhibits the greater surface area so far reported with well-defined mesoporous structure and electrical conductivity only one magnitude order smaller than the carbon material. Furthermore, electrochemical tests using ATO as support showed great stability to high overpotentials in acid media where the corrosion effect in carbon substrates is accelerated. Therefore, these experiments demonstrate the strong potential of the ATO support for using in several electrochemical applications as fuel cells, PEM-electrolysis, URFC and photoelectrolysis where the use of carbon is not suitable. It is expected that the use of in-house ATO support provide a good dispersion of electrocatalyst, reducing the electrocatalyst loading than those used by currently available commercial supports. Corrosion and stability experiments are carried out in order to get more intrinsic information of ATO; beside different electrocatalyst are supported for fuel cell and electrolysis evaluation.

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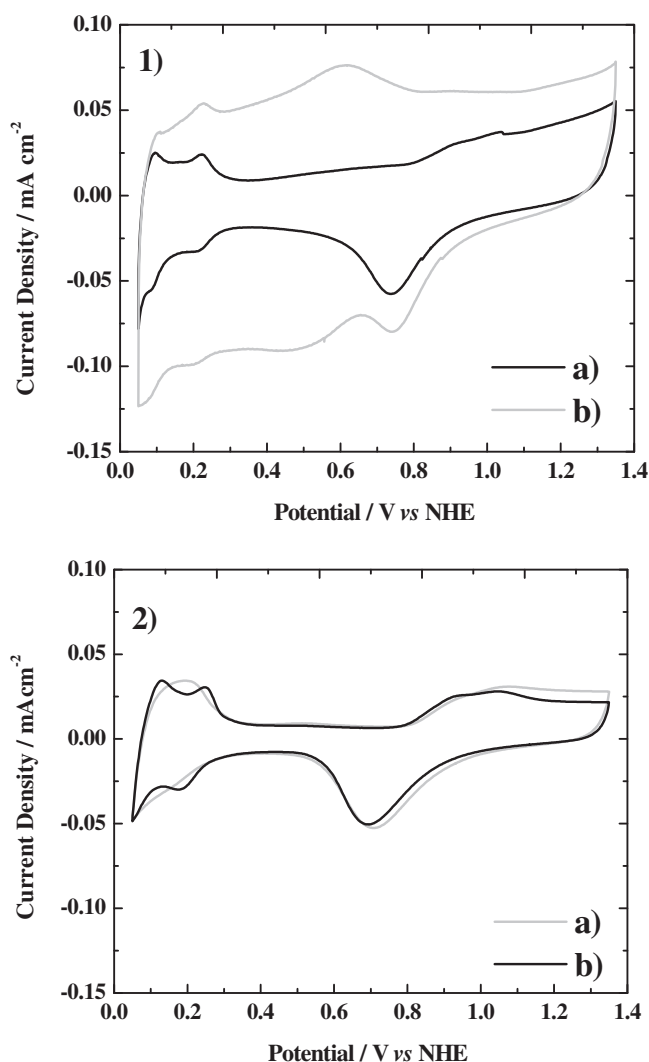


Fig. 3. Cyclic voltammograms of the catalysts 1) Pt/C and 2) Pt/ATO, a) before and b) after the stability test in  $\text{N}_2$  saturated 0.5 M  $\text{H}_2\text{SO}_4$  solution ( $20 \text{ mV s}^{-1}$ ).

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